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㉚ Improved zeolite ZK-5.

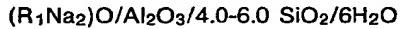
㉛ Zeolites having the ZK-5 structure but having a silica/
alumina ratio of up to 10 may be prepared by the use of
strontium in the synthesis gel, and such zeolites may be useful
in hydrocracking, reforming and separation.

EP 0 288 293 A2

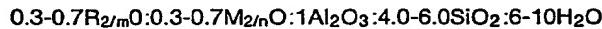
Description**IMPROVED ZEOLITE ZK-5**

This invention relates to zeolite ZK-5, its preparation and use in catalysis. In particular, it relates to zeolite ZK-5 containing and/or synthesized using, strontium.

5 Zeolite ZK-5 has been known for some time as a catalyst for cracking hydrocarbons as described in "Zeolite Molecular Sieves", D.W. Breck, pages 111-113, 180 it is described as an aluminosilicate of the formula:



10 (where R is derived from 1,4-dimethyl-1,4-diazocyclo [2.2.2] octane). US-A-3247195 and US-A-4001106 describe ZK-5 as having a composition in terms of mole ratio of oxides as:



15 where R is as defined above or a mixture with hydrogen and m is the valence of R, and M is a metal of valence n. In US-A-3247195 ZK-5 is reported as having an X-ray diffraction pattern with the following d(A) values and intensities:

	<u>d (A)</u>	<u>Relative Intensity (I/I₀)</u>
	13.3	18
20	9.41	100
	6.62	6
	5.93	41
25	5.41	48
	5.03	2
	4.69	6
30	4.41	50
	4.19	34
	3.93	22
35	3.81	18
	3.66	6
40	3.41	13
	3.21	35
	3.02	28
45	2.94	21
	2.81	26
	2.75	9
50	2.64	11
	2.59	2
55	2.54	9
60		

The preparation of zeolite L described in Inorganic Chemistry, Vol.5, No.9, September 1966, pages

1539-1541 comprises crystallizing the zeolite from a reaction mixture comprising mole ratios:
 $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 + \text{RO}/\text{Al}_2\text{O}_3$ 6-19

$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ 1.5-2.3

$\text{SiO}_2/\text{Al}_2\text{O}_3$ 4-11

$\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ 200-700

US-A-4001106 describes a preparation from an aqueous solution of oxides having a composition in terms of
 mole ratio of oxides as follows:

$\text{SiO}_2/\text{Al}_2\text{O}_3$ 2.5-15

$\text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{RO})$ 0.01-0.25

$\text{H}_2\text{O}/(\text{Na}_2\text{O} + \text{RO})$ 25-50

$(\text{Na}_2 + \text{RO})/\text{SiO}_2$ 1-2

at a temperature of 90°C-120°C.

"Synthesis and Nature of some salt-bearing Aluminosilicates" Barrer and Marcilly, J.C.S., Section A, pages 2735-2745 (1970) describes an alternative preparation via intermediate phases designated P(Cl), P'(Cl), Q(Cl), Q'(Br) which are in turn prepared by reaction of a barium halide upon a potassium or barium aluminosilicate gel, or on zeolite X, Y, analcite or chabazite.

US-A-4496528 describes a variation of this process in which zeolite P(Cl), P'(Cl), Q(Cl), Q'(Br) are extracted to remove barium ions. The product prepared in this way is of the formula:

0.5-0.9 $\text{M}_2\text{O}/0.2-0.5 \text{BaO}/\text{Al}_2\text{O}_3/2.5-7 \text{SiO}_2/0-0.3 \text{BaCl}_2/0-7 \text{H}_2\text{O}$

and has the following X-ray diffraction pattern:

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$d(\text{\AA})$	I/I_0
13.26	50
9.34	100
7.65	12
6.60	15
5.92	22
5.40	34
5.01	15
4.67	9
4.42	56
4.19	50
3.99	26
3.83	40
3.67	15
3.42	19
3.30	9
3.21	44
3.12	11
3.05	74
2.96	23
2.89	9
2.83	53
2.77	19
2.71	11
2.65	22
2.60	7
2.55	22

SU 1155564 discloses preparation of a (Na, Li) ZK-5 of the formula:

0.11-0.20Li₂O: 0.89-0.80Na₂O: Al₂O₃: 3.08-3.28SiO₂: 5-5.3H₂O

from a reaction mixture comprising the following mole ratios:

$$(Li_2O + Na_2O)/SiO_2 = 0.9-1.2$$

$$Na_2O/(Na_2O + Li_2O) = 0.45-0.7$$

$$H_2O/(Na_2O + Li_2O) = 60-75$$

$$SiO_2/Al_2O_3 = 5$$

US-A-3720753 describes a zeolite similar to ZK-5 having stoichiometric mole ratios of oxides, as follows:

0.1-0.4Cs₂O:0.6-0.9M₂O:Al₂O₃:YSiO₂:ZH₂O

wherein M may be either potassium or a mixture of potassium and sodium such that the ratio Na/K ≤ 1, and Z may be any value from 0 to about 10, and wherein Y is from 4 to about 7, preferably from 6 to about 7, and most preferably from greater than 6 to about 7.

The X-ray diffraction pattern of this zeolite is:

<u>d</u>	<u>I / I°</u>	20
13.39	47	
9.46	68	25
7.73	15	
6.68	30	
5.95	100	30
5.44	2	
5.04	6	
4.43	43	35
4.21	47	
3.84	51	
3.69	9	40
3.43	53	
3.22	60	
3.13	9	45
3.04	26	
2.96	32	
2.89	4	50
2.83	53	
2.65	15	
2.55	34	55

This synthetic zeolite, having pores within the range of 3 to 5.5 Å units, and in its purest form from 3 to 4 Å units, is prepared from an aqueous reaction mixture containing silica, alumina, and either a mixture of potassium oxide and cesium oxide, or potassium oxide, cesium oxide and a small amount, i.e. preferably less than about 3 percent, of sodium oxide. The proportions of these reactants in the initial reaction mixture are determined from the following molar ratios:

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Reactant Molar Ratios

5		<u>Broad</u>	<u>Preferred</u>	<u>Particularly Preferred</u>
10	$\text{SiO}_2/\text{Al}_2\text{O}_3$	3-12	5-10	7-9
	$\text{K}_2\text{O}+\text{Cs}_2\text{O}/\text{SiO}_2$	0.20-0.40	0.25-0.32	about 0.30
	$\text{Cs}_2\text{O}/\text{K}_2\text{O}+\text{Cs}_2\text{O}$	0.05-0.35	0.10-0.30	0.15-0.25
15	$\text{Na}_2\text{O}/\text{K}_2\text{O}+\text{Cs}_2\text{O}$	0-0.5	0-0.4	0-0.2
	$\text{H}_2\text{O}/\text{SiO}_2$	5-12	7-10	8-9

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It has now been found that a new form of zeolite ZK-5, capable of being more siliceous than the prior art forms, and containing strontium may be prepared directly from a reaction mixture containing strontium.

Thus, in one aspect the invention provides a zeolite having the formula:

25 0.9-1.3[(1-x) $\text{M}_{2/n}\text{O}+x\text{SrO}$]: Al_2O_3 : 4-10 SiO_2 : 0-10 H_2O

(wherein M is a cation of valence n and x is from greater than 0 to 0.3) and having an X-ray diffraction pattern (CuK α) having the following characteristic d(A) values:

30 Table A 9.3 ± 0.1
 35 5.40 ± 0.03
 4.41 ± 0.03
 4.18 ± 0.03
 3.98 ± 0.02
 3.82 ± 0.02
 3.21 ± 0.02
 3.03 ± 0.02
 2.95 ± 0.01
 2.82 ± 0.01

40 and preferably having the following more prominent d(Å) values:

45 Table B 13.1 ± 0.2
 9.3 ± 0.1
 6.60 ± 0.04
 5.91 ± 0.04
 50 5.40 ± 0.03
 4.41 ± 0.03
 4.18 ± 0.03
 3.98 ± 0.02
 3.82 ± 0.02
 3.66 ± 0.02
 3.21 ± 0.02
 3.03 ± 0.02
 2.95 ± 0.01
 2.82 ± 0.01
 55 2.64 ± 0.01
 2.54 ± 0.01

60 In a preferred aspect the zeolite is of the formula:

65 0.7-1.1 $\text{M}'_{2/n}\text{O}$: 0.001-0.3 SrO : Al_2O_3 : 6-10 SiO_2 : 0-10 H_2O

65 wherein M' is an alkaline earth or alkali metal of valence n.

The zeolite of the invention has the structure of zeolite ZK-5 but differs in that higher silica/alumina ratios may be prepared than have previously been reported. Thus in a further aspect this invention provides zeolite ZK-5 having a silica/alumina ratio of greater than 7, preferably from 7.5 to 10.

The zeolites also differ from reported forms of zeolite ZK-5 in containing strontium. It has been noted that the intensity of some of the characteristic lines of ZK-5 differ from those previously quoted for ZK-5, and this is believed at least in part to be a result of the presence of strontium. In another aspect this invention provides a zeolite ZK-5 containing strontium, whether introduced by synthesis, impregnation or ion exchange but preferably where the strontium is introduced by synthesis.

In a particularly preferred aspect of the invention the cation M or M' is or includes the potassium ion. Thus, in another aspect the invention provides zeolite ZK-5 in the potassium form - that is, of the formula:



Notwithstanding the preference for the potassium form of ZK-5, it may be desirable to include small amounts of other ions in addition to the preferred potassium in the synthesis of ZK-5 such as other alkali metals, alkaline earth metals. In addition, the synthesized potassium form of ZK-5 may be impregnated or exchanged with other ions to remove or replace at least a part of the potassium therein.

The zeolite of the invention displays an X-ray diffraction pattern typical for zeolite ZK-5, subject to the changes in position and intensity of the X-ray as may be expected to result from ion exchange, or different ratios of elements within the zeolite. Additional lines not belonging to the pattern for zeolite ZK-5 may appear in a pattern. This is an indication that one or more additional crystalline materials are mixed with zeolite ZK-5 in the sample being tested. It is a preferred feature of the invention that the amount of such additional crystalline materials is minimised in the zeolite material as synthesized. In particular, it is preferred that the synthesis of the zeolite of the invention is conducted so that the amount of zeolite W or zeolite L in the product of the synthesis is minimised.

The zeolites of the invention are preferably aluminosilicates and will be described hereinafter in terms of aluminosilicates, though other elemental substitutions are possible, for example aluminium may be substituted by gallium, boron, iron and similar trivalent elements, and silicon may be substituted by elements such as germanium or phosphorus.

The zeolites of the invention may be hydrated, typically with up to 10 moles of water per mole of Al₂O₃. When used as a catalyst base, as described hereinafter, the zeolite of the invention is preferably first calcined to remove water. In normal preparation from aqueous gels a hydrated form is first prepared and this may be dehydrated by heating.

The invention also provides a process for the preparation of zeolite ZK-5, in which an alkaline reaction mixture comprising water, a source of a metal M, a source of silicon, a source of aluminium and a source of strontium, with a composition falling within the following molar ratios (expressed as oxides):

$$(\text{M}_2\text{O} + \text{SrO})/\text{SiO}_2 \quad 0.16 - 0.30$$

$$\text{H}_2\text{O}/(\text{M}_2\text{O} + \text{SrO}) \quad 25 - 120$$

$$\text{SiO}_2/\text{Al}_2\text{O}_3 \quad 8 - 12$$

$$\text{SrO/SiO}_2 \quad 0.001 - 0.03$$

(wherein M is as defined hereinbefore, preferably potassium) is heated to a temperature of from at least 75°C and preferably from 100°C to 250°C, more preferably from 120°C to 225°C.

The principal components to the reaction mixture or synthesis gel are thus generally:

aluminium

silicon

alkali metal, preferably potassium

strontium

water

and optionally one or more additional metals as described hereinbefore and the relative proportions of these components and the chosen reaction conditions are important if the desired zeolite of the invention is to be obtained.

Thus, the zeolites of the invention are preferably obtained within the following preferred ranges:

$$(\text{K}_2\text{O} + \text{SrO})/\text{SiO}_2 \quad 0.17 - 0.25$$

$$\text{H}_2\text{O}/(\text{K}_2\text{O} + \text{SrO}) \quad 50 - 120$$

$$\text{SiO}_2/\text{Al}_2\text{O}_3 \quad 8 - 12$$

$$\text{SRO/SiO}_2 \quad 0.002 - 0.025$$

In addition to varying the proportions of the reactants in the reaction mixture, it is possible to vary the reaction conditions and in particular the crystallisation temperature. By using different temperatures, it may be possible to deviate further from the desired product. In general, within the broad reactant ratios defined for the process of the invention, a higher crystallisation temperature enables the silicon content to be lowered and/or the water content to be lowered and/or the potassium content (and thus the alkalinity) to be raised.

In the synthesis of the zeolite of the invention, the source of silicon for the reaction mixture is generally silica, and this is usually most conveniently in the form of a colloidal suspension of silica such as Ludox HS 40 available from E.I. Dupont de Nemours and Co. Colloidal silica sols are preferred since they result in less contaminating phases. However, other forms such as silicates may be used.

The source of aluminium may be an alumina introduced into the reaction medium as, for example, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, previously dissolved in alkali. However, it is also possible to introduce aluminium in the form of the metal, which is dissolved in alkali.

5 The zeolites of the invention are preferably obtained from reaction mixtures containing potassium. This potassium is preferably introduced as potassium hydroxide.

The source of strontium is preferably strontium hydroxide though other convenient strontium compounds such as the nitrate, carbonate, oxide or sulphate may be used.

10 The product of the processes described above is a mixed cation form of the zeolite containing alkali metal, preferably potassium, and strontium. By ion exchange of the product in the manner conventional to zeolite chemistry, other cations can be introduced.

It is also possible to add small amounts of other bivalent metal cations to the synthesis gel, such as barium, magnesium and other alkaline earth metals, copper, manganese, chromium, lead, iron, cobalt, nickel and zinc. These cations present in amounts as small as 1 to 1000 ppm may have effect in promoting formation of zeolite ZK-5.

15 Crystallisation time is related to the crystallisation temperature. The crystallisation is preferably carried out in the region of 150°C and at this temperature the crystallisation time may be from 24 to 160 hours, typically from 72 to 130 hours. Lower temperatures may require much longer times to achieve good yield of the desired product.

20 The crystallisation is generally carried out in a sealed autoclave and thus at autogenous pressure. Lower pressure will require longer crystallisation times.

Following the preparation as described above the zeolite ZK-5 may be separated, washed and dried in the normal manner.

25 The ability of the above process to produce zeolite ZK-5 is surprising since in the absence of strontium, the preparation would be expected to form zeolite L, as described in EP-A-96479, or zeolite W or a mixture depending upon the alkalinity of the synthesis gel.

30 The products of the processes of the invention described herein before are preferably substantially free from contaminant crystalline and amorphous materials. However, in employing these products in catalytic applications it may be desired to combine them with additional crystalline or amorphous materials as binders and this invention extends to such combinations. Thus, the invention extends to catalysts comprising a zeolite of the invention and a binder.

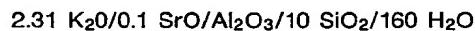
35 Zeolite ZK-5 is known to be useful as a cracking catalyst, for example in selective hydrocracking of linear paraffins or in reforming, and the zeolites of the invention may also be used in such applications, where the higher silica/alumina ratios obtainable in the invention may be advantageous. Other suitable applications are recovery of linear paraffins, clean-up of organic compounds such as linear paraffins or xylenes by selective removal of contaminants, and separation of propene from propane.

40 The catalysts of the present invention are also suitable for use in fluid catalytic cracking wherein a relatively heavy petroleum feedstock (BP 218-566°C) is converted to lower boiling products, usually in the heating oil or gasoline (or lighter) range. Typical fluid catalytic cracking conditions include a temperature range of from 466 to 510°C, with oil feed temperatures from 316 to 454°C, and regenerator exit temperatures for catalyst from 593 to 677°C.

45 The following Examples are now given though only by way of illustration to show certain aspects of the invention in more detail.

Example 1: Preparation of Zeolite ZK-5 using Strontium

50 A synthesis gel was prepared from potassium hydroxide pellets (87.3%), aluminium hydroxide powder, strontium hydroxide octahydrate, Ludox HS-40 (a silica colloid) and demineralised water to give a molar composition of:



55 In the absence of strontium this gel would crystallize to form zeolite L. Instead the gel was crystallized for 91 hours at 150°C in a 300 ml stainless steel autoclave, washed and dried and examined by XRD. The product was highly crystalline and had XRD-pattern of zeolite ZK-5. The X-ray data is given below:

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Table C

<u>d(A)</u>	<u>Relative Intensity</u>
13.14	22
9.32	100
6.60	26
5.89	24
5.39	35
5.00	18
4.67	7
4.40	102
4.17	86
3.98	34
3.21	47
3.66	23
3.41	16
3.20	53
3.03	87
2.95	36
2.82	80
2.75	12
2.64	37
2.59	10
2.54	39

Unit cell dimension

a = 18.68 Å

Examples 2 and 3; Comparative Examples A and B

The synthesis of Example 1 was repeated with various amounts of Sr in the synthesis gel. In these syntheses the Sr content was varied from 0.45 to 0.006 wt %. The gel compositions tested were in the range:

5 2.30 K₂O/(0.2 - 0.0025) SrO/Al₂O₃/10 SiO₂/160 H₂O

save that in Comparative Example B the amount of K₂O was increased to 2.50 in the above expression.

10 The gels were aged in 300 ml stainless steel autoclaves for 69 hours at 150°C to bring about crystallization.

10 After washing and drying the products were examined by X-ray diffraction. The products identified in the X-ray patterns are given below:

15	<u>Sr content in gel</u>		<u>Zeolite product obtained</u>
	molar ratio	wt %	XRD
20	Example	SrO/ SiO ₂	Sr
	2	0.02	0.45
25	3	0.0025	0.05
	A	0.0005	0.01
	B	0.00025	0.006

30 These results show that in this type of synthesis gel as little as 0.05 wt % of Sr species is sufficient to obtain pure zeolite ZK-5 according to the invention, while at lower amounts zeolite L is formed.

Examples 4-9: Synthesis using low alkalinity synthesis gels

35 To investigate a possible further increase in the SiO₂/Al₂O₃ ratio in the product the procedure of Example 1 was repeated with low alkalinity synthesis mixtures. Some of these synthesis gels were also seeded with traces of Ba; this was done to investigate whether it is possible to increase the formation rate of ZK-5, since this effect has been observed in the synthesis of zeolite L. In these syntheses the product yield was accurately measured because an increase in product yield will indicate an increased siliceousness of the product. The results are given below:

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Example	K_2O/SiO_2 molar ratio	Product Characteristics			Yield % a)
		XRD phase	% cryst.	SiO_2/Al_2O_3	
4	0.23b)	ZK-5	100c)		7.1 17.4
5	0.20b)	ZK-5	129		
6	0.18b)	ZK-5	93		18.6 19.4
7	0.18	ZK-5	74		19.8
8	0.16	ZK-5d)	n.a. e)		n.a. n.a.
9	0.26	ZK-5d)	n.a.		

- a) product yield: wt ratio dry product/gel X 100.
 b) gels were seeded with Ba(OH)₂/10 SiO₂ ratio 0.005).
 c) arbitrarily set at 100%.
 d) some contaminant present.
 e) not available.

These experiments show that ZK-5 can crystallize from extremely low alkaline synthesis mixtures, and that traces of Ba seems to enhance the formation of ZK-5. Reducing the gel alkalinity tends to increase the product yield and the SiO₂/Al₂O₃ ratio.

5 Certain of the zeolite ZK-5 products of the invention were analysed for elemental composition. The results
are given below:

10	Example	Product Composition		
		K/Al	SiO ₂ /Al ₂ O ₃	Sr content wt %
		molar ratios		
15	2	1.05	7.1	2.26
	3	0.95	6.7	0.25
20	6	1.07	8.4	1.05

25 The product of Example 2 was tested and its n-hexane adsorption was measured at 11.6% at p/Po=0.5,
T=30°C.

30 **Claims**

1 A zeolite having the formula:

35 0.9-1.3[(1-x)M_{2/n}O + xSrO]: Al₂O₃: 4-10 SiO₂: 0-10 H₂O

(wherein M is a cation of valence n and x is from greater than 0 to 0.3) and having an X-ray diffraction pattern (CuK α) having the following characteristic d(Å) values:

40 Table A 9.3 ± 0.1

5.40 ± 0.03
4.41 ± 0.03
4.18 ± 0.03
3.98 ± 0.02
3.82 ± 0.02
3.21 ± 0.02
3.03 ± 0.02
2.95 ± 0.01
2.82 ± 0.01

50 2. A zeolite as claimed in claim 1, having the following more prominent d(Å) values:

Table B 13.1 ± 0.2

55 9.3 ± 0.1
6.60 ± 0.04
5.91 ± 0.04
5.40 ± 0.03
4.41 ± 0.03
4.18 ± 0.03
3.98 ± 0.02
3.82 ± 0.02
3.66 ± 0.02
3.21 ± 0.02
3.03 ± 0.02
2.95 ± 0.01

2.82 ± 0.01

2.64 ± 0.01

2.54 ± 0.01

3. A zeolite as claimed in claim 1 or claim 2 of the formula:

0.7-1.1 M'_{2/n}O: 0.001-0.3 SrO: Al₂O₃: 6-10 SiO₂: 0-10 H₂O

5

wherein M' is an alkaline earth or alkali metal of valence n.

4. Zeolite ZK-5 having a silica/alumina ratio of greater than 7.

5. Zeolite ZK-5 having a silica alumina ratio of from 7.5 to 10.

6. Zeolite ZK-5 containing strontium.

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7. Zeolite ZK-5 as claimed in claim 6 where the strontium is introduced by synthesis.

8. Zeolite ZK-5 of the formula:

0.7-1.1 K₂O: 0.001-0.3 SrO: Al₂O₃: 6-10 SiO₂: 0-10 H₂O

15

9. A process for the preparation of a zeolite as claimed in any of claims 1 to 8, in which an alkaline reaction mixture comprising water, a source of a metal M, a source of silicon, source of aluminium and a source of strontium, with a composition falling within the following molar ratios (expressed as oxides):

M_{2/n}O + SrO/SiO₂ 0.16 - 0.30H₂O/(M_{2/n}O + SrO) 25 - 120SiO₂/Al₂O₃ 8 - 12

20

SrO/SiO₂ 0.001 - 0.03

(wherein M is as defined in claim 1) is heated to a temperature of from at least 75°C.

10. A process as claimed in claim 9, in which the reaction mixture is heated to from 120°C to 225°C.

11. A process as claimed in claim 9, in which the reaction mixture has a composition within the following preferred ranges.

25

(K₂O + SrO)/SiO₂ 0.17 - 0.25H₂O/(K₂O + SrO) 50 - 120SiO₂/Al₂O₃ 8 - 12SrO/SiO₂ 0.002 - 0.025

12. A process as claimed in claims 9 to 11, in which the reaction mixture comprises 1 to 1000 ppm of one or more of barium, magnesium, manganese, chromium, copper, lead, iron, cobalt, nickel and zinc.

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13. A catalyst comprising a zeolite as claimed in any of claims 1 to 8 and a binder.

14. The use of a zeolite claimed in any of claims 1 to 8 in selective hydrocracking of linear paraffins, in reforming, in recovery of linear paraffins, in clean-up of organic compounds by selective removal of contaminants, or in separation of propene from propane.

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15. The use of a zeolite as claimed in any of claims 1 to 8 in fluid catalytic cracking of heavy petroleum feedstock (boiling point in the range 218 to 566°C) to lighter boiling products.

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EUROPEAN PATENT APPLICATION

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C 10 G 11/05

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㉛ Improved zeolite ZK-5.

㉜ Zeolites having the ZK-5 structure but having a silica/
alumina ratio of up to 10 may be prepared by the use of
strontium in the synthesis gel, and such zeolites may be useful
in hydrocracking, reforming and separation.

EP 0 288 293 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 30 3634

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim			
A	GB-A-1 297 140 (B.P.) ---		C 01 B 33/28		
A	GB-A-1 135 938 (UNION CARBIDE) ---		B 01 J 29/28		
A	GB-A-1 183 000 (UNION CARBIDE) ---		C 10 G 47/16		
A	DE-A-3 518 094 (DIRECTOR GENERAL, AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY) -----		C 10 G 11/05		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)		
			B 01 J 29/00		
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Examiner			
THE HAGUE	23-09-1988	DEVISME F.R.			
CATEGORY OF CITED DOCUMENTS					
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document					
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document					